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Abstract
Satellites on the low-binding-energy side of core-level photoelectron emission due to extra 4f screening are a well-known feature in the x-ray photoelectron spectra of valence fluctuation materials and rare-earth metals. A notable exception is Eu metal, where up to now no low-binding-energy satellite has been observed. In this paper we show that in Eu metal the 4d–4f resonance can decay via a resonant Auger decay, which is not a constant kinetic-energy feature due to a rapid change of the strength of 4f screening with excitation energy, establishing a low-binding-energy replica of the 5p core-level photoelectron emission.

Keywords
Ames Laboratory, valence fluctuation, Auger decay

Disciplines
Atomic, Molecular and Optical Physics | Condensed Matter Physics | Physics

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ARTICLES

Evidence for replicate $5p$ core levels in photoelectron spectra of Eu metal due to nonconstant kinetic-energy resonant Auger decay

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Satellites on the low-binding-energy side of core-level photoelectron emission due to extra $4f$ screening are a well-known feature in the x-ray photoelectron spectra of valence fluctuation materials and rare-earth metals. A notable exception is Eu metal, where up to now no low-binding-energy satellite has been observed. In this paper we show that in Eu metal the $4d$-$4f$ resonance can decay via a resonant Auger decay, which is not a constant kinetic-energy feature due to a rapid change of the strength of $4f$ screening with excitation energy, establishing a low-binding-energy replica of the $5p$ core-level photoelectron emission.
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Replicate core levels are a well-known feature in the x-ray photoelectron spectra of the valence fluctuation compounds of Ce, Sm, Eu, Tm, and Yb,[1,2] and the rare-earth metals.[3,4] In both cases the low-binding-energy replica (''satellite'' emission) of the ''main'' core level emission is caused by the occupation of unfilled f levels, leading to an enhanced screening of the core hole and therefore photoemission at higher kinetic energy compared to the main line. While in the valence-fluctuation compounds the occupation of the f levels of an ion fluctuates spontaneously between f^n and f^{n+1} on a time scale longer than that characteristic of the photoemission process ($\sim 10^{-16}$ s), the change of the occupation number of the f levels in the rare-earth metals is a consequence of the photoionization process itself, as photoionization has the same effect on the unoccupied f levels as a unit increase of the nuclear charge, lowering the energy of the empty $4f$ level.[3] For the rare-earth metals it has been shown that the attractive interaction of a $3d$ core hole with empty $4f$ levels can be strong enough to pull the $4f^{n+1}$ configuration (with $4f^n$ the ground-state configuration) below the Fermi level.[3] The low-binding-energy replica of the $3d$ main line then corresponds to a $4f^{n+1}$ configuration in the final state, because of better screening of the $3d$ core hole due to the additional $4f$ electron, while in the case of the main line the $3d$ core hole is screened by valence-band (VB) electrons and the $4f^n$ configuration is retained in the final state.[3] The only rare-earth metal where a low-binding-energy satellite has not been observed up to now is Eu metal. The reason for this is the high stability of its f^7 ground-state configuration which makes it impossible to populate unoccupied $4f$ levels even under the influence of a $3d$ core hole.[4] Theoretical[5,6] and experimental[7] studies of the $4f$ excitation energies of the rare-earth metals have indeed shown that the energy required for a $4f^n$ to $4f^{n+1}$ excitation not only reaches a maximum but is by far the largest for Eu metal, whose f^8 configuration lies ~ 8.6 eV above the Fermi level.

Another possibility for populating the unoccupied $4f$ levels of rare-earth metals is to excite $4d$ electrons resonantly into the unoccupied $4f$ levels by tuning the photon energy through the $4d$-$4f$ threshold. The resonant excitation of $4d$ electrons into unoccupied $4f$ levels not only leads to a strong enhancement of the photon absorption cross section, but has also an impact on the photoelectron spectra, depending on the channel into which the $4d$ hole decays. A $4d$-$4f$ resonance in a rare-earth metal can decay in two principal ways: (a) Resonant or nonresonant Auger decay: in the latter case the electron excited upon the $4d$-$4f$ resonance tunnels through the potential barrier, leading to a singly positive ionized state due to the $4d$ core hole which then predominantly decays via an Auger process,[8] while in a resonant Auger decay it remains as a spectator during the recombination process. The spectator $4f$ electron affects the kinetic energy of the outgoing electrons, which leads to an energy shift with respect to a normal Auger decay having the same final state. (b) Autoionization: the electron excited upon the $4d$-$4f$ resonance fills the $4d$ core hole, leading to electron emission from the VB or the $5s$, $5p$, or $4f$ core levels. The final state after autoionization is the same as after direct photoemission from the VB or the $5s$, $5p$, or $4f$ core levels, which leads to a photon-energy-dependent modulation of the intensities of these levels in the photoelectron spectrum due to interference between direct emission and emission due to autoionization.

To induce a replicate core level via $4d$-$4f$ resonance, there would have to be a resonant Auger decay of the excitation which involves the core level and a level at lower binding energy but not the $4f$ levels. The main line would then be direct photoemission from the core level (no additional $4f$ electron due to the $4d$-$4f$ resonance), while its low-binding-energy replica would be the aforementioned resonant Auger decay because of the better core-hole screening due to the additional f electron in the final state. Up to now studies of the decay mechanisms of the $4d$-$4f$ resonant excitation in rare-earth metals have not revealed the existence of a decay channel which does not involve at least one f electron.[9–12] In this paper we will demonstrate that in the case of Eu metal the decay channels of the $4d$-$4f$ resonant

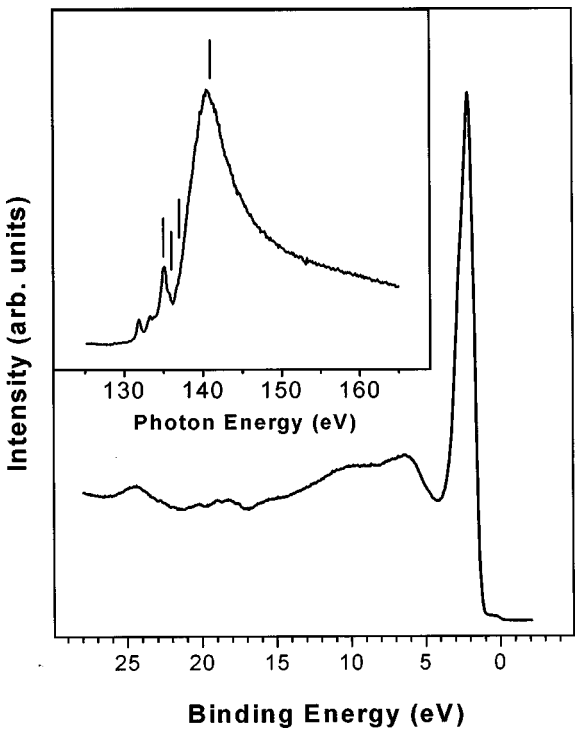

FIG. 1. EDC of Eu metal recorded using 141 eV photon energy. The inset shows the photoabsorption cross section of Eu metal around the 4d-4f resonance. The bars indicate the photon energies where the on-resonance spectra were recorded.

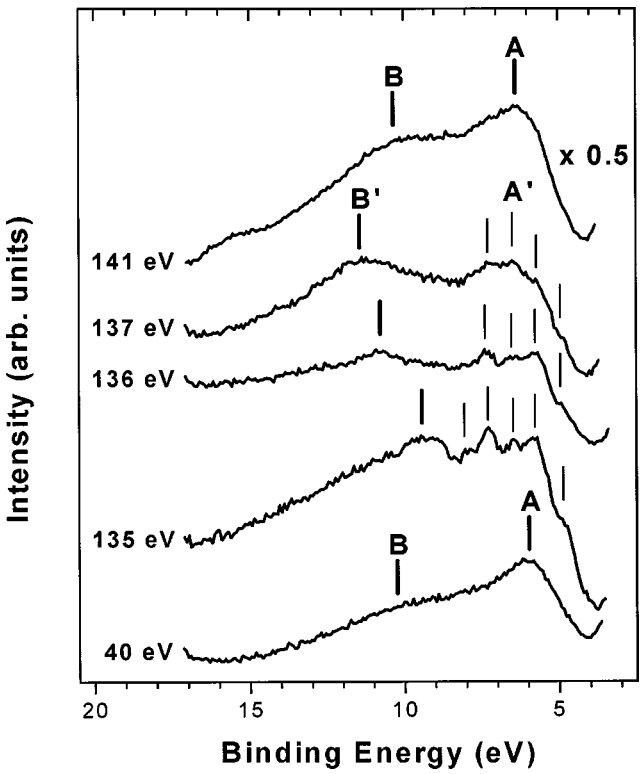

FIG. 2. Expanded-scale EDC's in the binding-energy range from 4 to 17 eV for spectra recorded off- and on-resonance. The EDC's are normalized to the photon flux. Note that the spectrum recorded using 141 eV is on a different intensity scale than the other EDC's.

excitation incorporate a resonant $N_{45}VO_{23}$ Auger decay [final state $5s^25p^54f^8(5d6s)^1$] which does not involve f electrons, is not a constant kinetic energy feature due to variation of the screening of the 4f electrons with excitation energy, and represents a low-binding-energy replica of the direct 5p [final state $5s^25p^54f^7(5d6s)^2$] core-level photoemission.

Vacuum outgassed Ames Laboratory Eu was evaporated as a polycrystalline film onto polycrystalline Ta and stainless-steel substrates. Pressures during evaporation did not exceed a few times 10^{-10} Torr, and measurements were made under pressures in the 10^{-11} Torr range. Photoelectron spectra were taken in the energy distribution curve (EDC) and constant-final-state (CFS) modes with an angle-integrating (cylindrical-mirror analyzer) electron spectrometer using synchrotron radiation from Aladdin as the source. The overall energy resolution was 200 meV.

The photoabsorption cross section of Eu metal in the region of the 4d-4f excitation is shown in the inset of Fig. 1 which was obtained by measuring the yield of secondary photoelectrons (CFS spectrum at 5 eV kinetic energy)[13] of a Eu film, and is in good agreement with the results of previous publications.[14] The absorption spectrum contains narrow peaks in a photon energy region from 130 to 137 eV and a broad, strong maximum at 141 eV, which in the following will be referred to as the fine structure and the giant resonance, respectively. EDC's were recorded at selected photon energies off- and on-resonance. The overall shape of the EDC's recorded off- and on-resonance is essentially the same, and in agreement with data reported in the literature;[11] an example recorded at 141 eV photon energy is shown in Fig. 1. One can easily identify emission due to the (5d6s) bands at the Fermi level, the unresolved 4f doublet at 2 eV binding energy, and two peaks due to the 5p doublet at $\sim$18.5 and $\sim$24.5 eV. Not yet addressed is the spectral intensity between 4 and 17 eV binding energy, which is present on- and off-resonance. The remainder of the paper is devoted to a detailed discussion of this structure.

In Fig. 2, expanded-scale EDC's recorded on- and off-resonance in the binding energy range from 4 to 17 eV are shown. It is evident that there is a difference between the spectra recorded in the fine structure of the 4d-4f excitation (EDC's recorded at 135, 136, and 137 eV photon energy) and the spectra recorded in the giant- (141 eV photon energy) or off-resonance (40 eV photon energy). The latter show two broad peaks at $\sim$6 and $\sim$10.5 eV binding energy (labeled A and B). These structures were also observed in earlier work and can be assigned to excited $4f^6$ final states (4f shake-ups) which are reached upon photoionization, in addition to the $4f^6$ ground state (the 4f main line at $\sim$2 eV).[11]

4f shake-ups may be also present in the EDC's recorded in and near the fine structure of the 4d-4f resonance, but inspection of the corresponding EDC in Fig. 2 reveals that the spectra are dominated by two features (labeled A' and B') which have another physical origin. The lowest-binding-energy structure is also at $\sim$6 eV, but shows, in contrast to its counterparts in the EDC recorded off-resonance or at giant resonance, a distinctive fine structure. The position of these fine-structure peaks is not dependent on photon energy. The second structure at higher binding energy, on the other hand, moves to higher binding energy with increasing photon energy, with the binding-energy increase roughly equaling

the increase in photon energy. This behavior is not compatible with that expected from a $4f$ shake-up, but rather suggests that feature B' is due to an Auger decay.

The observation of additional spectral structure in the EDC of Eu metal between the $5p$ and $4f$ emissions, which is only present for photon energies in or near the fine structure of the photoabsorption cross section, was also reported in earlier publications and for Gd metal, which also has a half-filled $4f$ shell in the initial state.[9,11] In these publications the extra structure is assigned to a resonant $N_{45}N_{67}N_{67}$ Auger decay. The difference between the final state after direct photoemission from a $4f$ level and after a resonant $N_{45}N_{67}N_{67}$ decay is that, in the former, all $4f$ electron spins are aligned parallel, while in the latter, the spin of the electron which was excited into an unoccupied $4f$ level by the resonance is aligned antiparallel to the other $4f$ electron spins.[9] This represents an excited state, and therefore there is a satellite on the high-binding-energy side of the direct $4f$ photoemission. Nonetheless, in the next paragraphs we will present evidence for a different explanation in terms of a $N_{45}N_{67}N_{67}$ nonresonant- and a $N_{45}VO_{23}$ resonant Auger decay in the case of Eu metal.

The $N_{45}N_{67}N_{67}$ Auger emission can be easily identified in the 135–137 eV EDC's as feature B', which, indeed, is a constant kinetic-energy feature having a kinetic energy of $\sim$120.5 eV (referenced to the vacuum potential) which is $\sim$0.5 eV lower than reported for the nonresonant $N_{45}N_{67}N_{67}$ Auger in Ref. 10. Despite this small difference we assign feature B' to a nonresonant rather than a resonant Auger decay for reasons which will become clear later. Feature A', on the other hand, shows a remarkable similarity in shape to the $5p_{3/2}$ emission (see Fig. 3). This strongly suggests that feature A' is a low-binding-energy replica of the direct photoemission from the $5p_{3/2}$ level due to enhanced screening of the $5p$ core hole provided by the $4f^8$ configuration reached upon the $4d$-$4f$ resonance. For this to be true the $4f^8$ configuration has to be retained in the final state which means that in the case of the low-binding-energy replica of the $5p$ emission, the energy necessary to eject an electron from a $5p$ level cannot be due to a $4f$-$4d$ transition but must be provided by the filling of the $4d$ hole by an electron from the $(5d6s)$ bands. Therefore we suggest that feature A' is due to a $N_{45}VO_{23}$ [V stands for the $(5d6s)$ bands] resonant Auger decay.[15] It is interesting to note that the splittings between replicate $3d$ or $4d$ core levels in the valence fluctuation materials ($\sim$10–11 eV)^2 come quite close to the observed splitting of the replicate $5p$ core levels of Eu metal ($\sim$12.7 eV).

One problem remains to be addressed: feature A' is not a constant kinetic-energy feature, as is expected for emission related to an Auger decay. One has to note, however, that the screening of the $5p$ core hole after the resonant $N_{45}VO_{23}$ decay [final state $4d^{10}5s^25p^54f^8(5d6s)^1$] is photon energy dependent, as the $4d$ electron is excited into higher-lying unoccupied $4f$ levels with increasing photon energy. This may lead to a photon-energy-dependent change in the screening capability of this $4f$ electron in the $4f^8$ final state. After a normal Auger decay feature A' would be expected to be at 2 eV higher binding energy in the 137 eV EDC than in the 135 eV EDC. This implies that if our designation of feature A' to a resonant Auger decay is to be correct, the screening effect due to the $4f$ electrons in the final state has to improve by $\sim$2 eV from 135 to 137 eV photon energy. For this to be the case the charge density related to the electron excited into an unoccupied $4f$ level in the $4d$-$4f$ resonance has to contract rapidly with rising excitation energy (i.e., upon approaching the giant resonance), thus creating a higher charge density between the $5p$ core hole and the charge of the nucleus and hence improved screening.

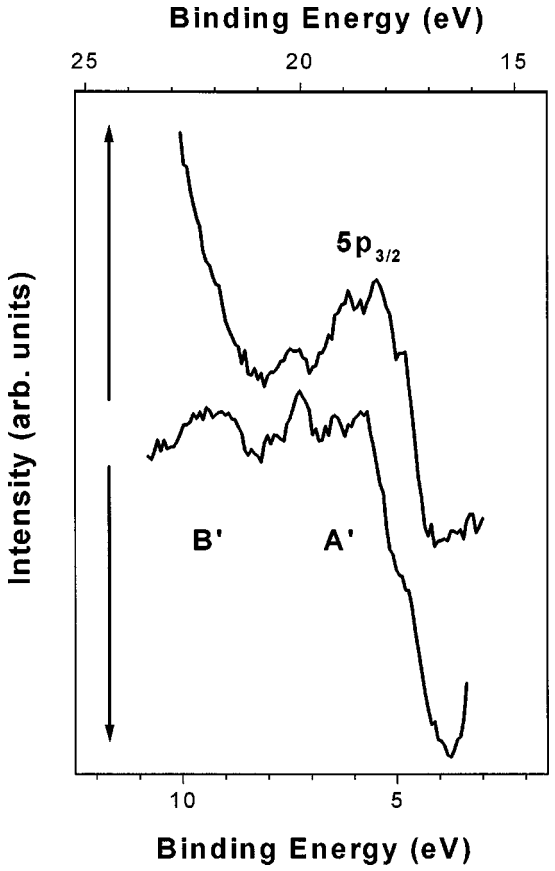

FIG. 3. Comparison of feature A' and the $5p_{3/2}$ emission in the 135 eV EDC. Lower- and higher-binding-energy scales are for the lower and upper curves, respectively.

It has been shown that in the case of rare earths the $4f$ levels experience a double-well potential.[16] The outer well is broad and shallow, and can accommodate an infinite Rydberg series of bound $4f$ levels which have little overlap with the more localized $4d$ levels. The inner well, on the other hand, is narrow and deep, and can only accommodate a small number of bound $4f$ levels which have a large overlap with the $4d$ levels. In the $4d^94f^8$ configuration the $4f$ levels are spread due to exchange splitting with the $4d$ hole. Due to the large $4d$-$4f$ overlap the $4f$ multiplets in the inner well are spread over a much wider energy range than the outer-well $4f$ levels, with some multiplets raised far above the threshold where they broaden due to autoionization.[17] Calculations have shown that in the case of a $4f$ shell not nearly filled (i.e., for Eu) the oscillator strength of the $4d$-$4f$ excitation is concentrated into transitions to the higher-lying $4f$ levels, i.e., to inner well $4f$ levels raised far above the threshold, in the giant resonance.[17] Thus for excitation energies in the fine

structure of the $4d$-$4f$ resonance the wave function of the electron excited into an unoccupied $4f$ level in the $4d^9 4f^8$ intermediate-state configuration resides predominantly in the outer well but rapidly contracts into the inner well (i.e., becomes more localized) for excitation energies approaching the giant resonance. Due to the fast time scale of a resonant $N_{45}VO_{23}$ Auger process and the noninvolvement of $4f$ electrons in this particular decay, it is reasonable to assume that the spatial localization of the $4f$ electrons in the intermediate state is essentially retained into the $5p^5 4d^{10} 4f^8 (5d6s)^1$ final state, thus yielding an excitation-energy-dependent screening of the $5p$ core hole. Finally, one should note then that for the same reason the screening of the resonant $N_{45}N_{67}N_{67}$ Auger decay should be dependent on the excitation energy. This is not observed in the case of feature B', and thus justifies our assignment of feature B' to a nonresonant $N_{45}N_{67}N_{67}$ Auger decay for photon energies in the fine structure of the photoabsorption cross section. In the light of these results the assignment of a constant kinetic energy to a resonant Auger decay has to be regarded as non-trivial.

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[15] The corresponding nonresonant $N_{45}VO_{23}$ Auger in Eu metal has a $4d^{10}5s^2 5p^5 4f^7 (5d6s)^1$ final state, and would be expected to have $\sim$10 eV lower kinetic energy (i.e., $\sim$115 eV). In Ref. 10 electron emission close to 115 eV is indeed reported, although it is assigned to be due to a $N_{45}N_{67}$-$N_{67}N_{67}N_{67}$ satellite to the $N_{45}N_{67}N_{67}$ Auger decay.
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